Calculated Magnetic and Electronic Properties of Pyrochlore Iridates

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Using density functional theory and LDA+U method, we investigate magnetic and electronic structure of $Y_2Ir_2O_7$ and rare–earth based pyrochlore iridates. Our study reveals that the ground state is a non–collinear magnetic insulating state. Due to strong spin-orbit coupling in Ir $5d$, there is an unusual correlation between the bands near Fermi level and the magnetization direction, resulting in a possibility of insulator–to–metal transition under applied magnetic field. This makes pyrochlore iridates a good candidate for possible magnetoressitance and magnetooptical applications.

While it has been realized that the Coulomb interaction is of substantial importance in $3d$ transition metal systems, resulting in a great variety of their physical properties, such, e.g., as metal–insulator transition[1], colossal magnetoresistance[2] and high–T_c superconductivity[3], the $4d$ and the $5d$ orbitals are, on the other hand, spatially more extended and usually possess a much broader bandwidth, making the correlation effects to be minimal. However, very recently, both theory and experiment give the evidence on the importance of interplay between spin–orbit coupling and Coulomb interaction for several, mainly Ir based, $5d$ compounds, which have received a lot of research attention [4–14]. In particular, in Sr_2IrO_4, one of most studied Ir oxides, it has been found that the material becomes a Mott insulator [4, 5], and exhibits very interesting magnetoelectric properties[7]. A different system, $Na_4Ir_3O_8$, which crystallizes in a geometrically frustrated spinel structure, is an insulator with a large Curie–Wiess temperature (about 650 K) and with a considerable effective moment (1.96 μ_B)[15]. However, this compound does not exhibit any sign of magnetic order even for the lowest measured temperature[15], and it has been suggested as one of the few long sought quantum spin liquids[16–18]. There is also theoretical work that addresses anisotropy of magnetic interactions[19, 20].

Ir oxides $A_2Ir_2O_7$[6, 21–26] ($A=$ Y or rare–earth element), which crystallize in a pyrochlore structure[27], is another geometrically frustrated iridate system. It has been recently discussed in connection with a novel "topological Mott insulator" phase[14] seen between topological band insulating[28] and conventional Mott insulating[1] phases as interactions get stronger. Experiment observes that depending on the A–site, $A_2Ir_2O_7$ show a wide range of electrical properties [21–25]. For example, $Y_2Ir_2O_7$ is an insulator[6] but with increasing the ionic radius at the A–site, the system eventually becomes metallic for $Nd_2Ir_2O_7$[21], while $Pr_2Ir_2O_7$ shows strong Kondo behavior[25]. Moreover, it has been found that temperature will drive an insulator–to–metal transition associated with abnormal magnetic behavior without structural change[21]. There are also several electronic structure calculations trying to explore electronic and magnetic properties of the iridates with geometrically frustrated structure[19, 29].

In the present work, we perform a detailed study of the magnetic and electronic structure for $A_2Ir_2O_7$. We find that the ground state of those systems is a non–collinear magnetic state while geometrically frustrated pyrochlore lattice makes other states with different orientations of moments close in energy. When $A=$Pr and Nd the electronic structure of these compounds shows metallic behavior while for $A=$Y, Sm, Eu the materials are insulators. We uncover that spin–orbit (SO) coupling affects the energy bands near the Fermi level and depending on orientation of moments some of those systems can be switched from an insulator to a metal. Exotic electronic and magnetic properties would make Ir pyrochlore to be good candidates for various applications including magnetoresistance effect and magnetooptics.

We perform our electronic structure calculations based on local spin density approximation (LSDA) to density functional theory (DFT) with the full–potential, all–electron, linear–muffin–tin–orbital (LMTO) method[30]. We use LSDA+U scheme[31] to take into account the electron–electron interaction between Ir $5d$ electrons, and use U = 2 eV which has been previously found to be adequate in iridates[4, 5, 9]. When the A site is a rare earth element, we also add the Coulomb interaction for the localized $4f$ electrons and use U = 6 eV. We use a $12\times12\times12$ k–mesh to perform Brillouin zone integration, and switch off symmetry operations in order to minimize possible numerical errors in studies of various (non–)collinear configurations. We use experimental lattice parameters[24] in all set ups.

We first discuss our results for $Y_2Ir_2O_7$. Without spin orbit (SO) coupling, both LSDA and LSDA+U predict this system to be metallic which is not consistent with the experiment. Since the SO strength is large for Ir $5d$ electrons (about 0.4 eV)[32], and has been found to produce an insulating behavior in Sr_2IrO_4[4, 5], we have performed the LSDA+U+SO calculations. There are four Ir

atoms inside the unit cell forming a tetrahedral network as shown in Fig.1. We first set an initial magnetization axis along (001) direction, however the calculations converge to a non–collinear state with the magnetic moment departing from the initial orientation a little bit. The four Ir sites have similar spin and orbital moments (about 0.13 μ_B) and both of them are slightly smaller than theoretical values reported previously[29]. However, due to the obtained slight non–collinearity of the solution, the net magnetic moment is found to be small.

Each of four Ir atoms is octahedrally coordinated by six O atoms, which makes the Ir $5d$ state split into doubly degenerate e_g and triply degenerate t_{2g} states. Due to the extended nature of Ir $5d$ orbital, the crystal–field splitting between t_{2g} and e_g is large with the e_g band to be 2 eV higher than the Fermi level. The bands near the Fermi level are mainly contributed by Ir t_{2g} with some mixing with O $2p$ states. SO coupling has a considerable effect on these t_{2g} states: it lifts their degeneracy and produces 24 separate bands in the range from -2.3 to 0.7 eV. Same as in Sr_2IrO_4[4, 5], the bandwidth of these t_{2g} states in our LSDA+U+SO calculation for $Y_2Ir_2O_7$ is also narrow, however, it is still metallic as shown in Fig.2(a). Naively one may expect that using larger Coulomb U will result in an insulating state. However, our additional calculations show that increasing U cannot solve this problem, and even a quite large U (=5 eV) cannot open a band gap for the initial collinear (001) setup. Here we agree with the previous calculation[29], which also showed that U cannot open a band gap.

Strong spin–orbit coupling may however induce the dependence of the band structure on quantization axis. So, we subsequently perform our calculations with initial magnetization aligning along (110), (120), (111) directions. We also perform the calculations with two sites in a tetrahedron along and other two pointed oppositely to (001), (111), (110) or (120) direction in order to account for possible antiferromagnetism. Interestingly, we find that despite the strong SO coupling which usually results in a large magnetic anisotropy energy, for $Y_2Ir_2O_7$, the rotation of magnetization does not involve too much change in the total energy. Among the magnetic configurations mentioned above, the (111) direction is found to be lowest, but the energy difference between this and the highest energy (001) state is just about 3.7 meV per unit cell. It is also interesting that while the magnetization direction does have a considerable effect on the bands near the Fermi level, as can be seen from comparing the Fig.2(a) and Fig.2(b), it turns out that all of the above mentioned calculations converge to metallic states. Also, all of them produce a considerable net magnetic moment in contrast to the experiment [22–24]. Thus, one can conclude that neither of these magnetic configurations may be the ground state.

With the pyrochlore structure, the Ir sublattice has a topology consisting of corner–sharing tetrahedra and is

TABLE I: The spin $\langle S \rangle$ and orbital $\langle O \rangle$ moment (in μ_B), the total energy E_{tot} (in meV) as well as the band gap E_{gap} (in meV) for several selected magnetic configurations of $Y_2Ir_2O_7$.

Configuration:	(001)	(111)	2–in/2–out	all–in/out
$\langle S \rangle$	0.13	0.17	0.14	0.13
$\langle O \rangle$	0.13	0.13	0.15	0.17
E_{tot}(meV)	4.47	0.69	3.21	0.00
E_{gap}(meV)	0	0	0	30

geometrically frustrated. Thus, we carry out several non–collinear calculations with the initial state to be "all–in/out" (where all moments point to or away from the centers of the tetrahedron), "2–in/2–out" (two moments in a tetrahedron point to the center of this tetrahedron, while the other two moments point away from the center, i.e. the spin–ice[33] configuration), and "3–in/1–out" magnetic structures (see Fig.1 for the moments configuration). We find that the "all–in/out" configuration is the ground state, and this state is insulating as shown in Fig.2(c): it has a band gap of 0.03 eV. The experimental band gap for $Y_2Ir_2O_7$ is not available, though it had been expected that it should be larger than that of $Sm_2Ir_2O_7$ (0.01 eV)[21]. Different from other magnetic configurations, during the self–consistency the "all–in/out" state will retain their initial input direction; thus, there is no net magnetic moment. This is consistent with the experimental fact on the absence of the magnetic hysteresis loop[24]. As shown in Table I, the energy difference between the ground and several selected excited states with different orientations of moments is small. Here, the energy difference involves not only the energy of magnetic anisotropy but also the effect of intersite exchange interaction. Due to the geometrically frustrated structure this energy difference is obviously smaller than that found for another $5d$ compound Ba_2NaOsO_6[12].

Regardless the proximity of the ground and excited (or said metastable) states in energy, they would have very different conductivity and magnetic properties. Thus one can understand that for the same compound $Y_2Ir_2O_7$ Taira et $al.$[24] observe no ferromagnetic ordering while Yanagishima et $al.$[22, 23] claim a presence of a small net magnetic moment. One can also understand the observed temperature induced metal–insulator transition, as well as a large difference in temperature dependence of magnetization measured under zero–field–cooled conditions (ZFC) and under field–cooled conditions (FC) at low T's.

Based on both strong sensitivity of the energy bands near the Fermi level on the orientation of moments, and proximity of various magnetic states in energy, it is natural to expect that an application of a magnetic field could have a big effect not only on the magnetic response but also on the conductivity in iridates. In particular, this should result in a large magnetoresistance effect if one is
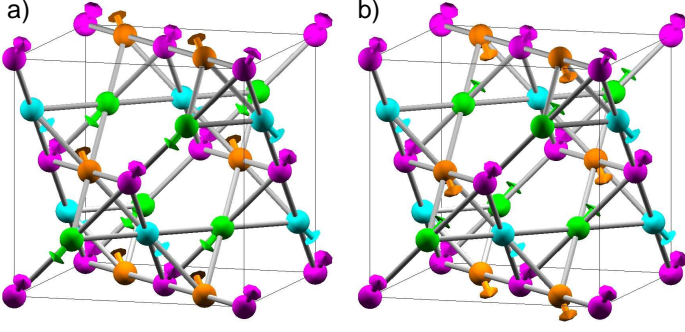
FIG. 1: The pyrochlore structure showing Ir tetrahedral network and its magnetic configurations (a) "all–in/out" configuration. (b) "2–in/2–out" configuration. The arrows denote moments directions.

able to switch between insulating "all–in/out" state and any collinear state. This simple idea has been proved by the following numerical calculation. Starting from the "all–in/out" ground state, we apply an external field along (001) direction. The result shows that the external field will rotate the magnetic moments meanwhile only slightly change their magnitude. A 5 T magnetic field along (001) induces a 0.07 μ_B net magnetic moment, which is in fact close to the experiment performed for $Sm_2Ir_2O_7$, where it was shown that a 4 T magnetic field produces a 0.05 μ_B total moment[24]. Increasing the field further, the numerical calculation does find energy bands crossing the Fermi level, namely an insulator–to–metal transition at a field of 40 T, although there is already non–negligible density of states at E_f for a lower magnetic field.

Another interesting feature which emerges from this electronic structure is an expected magnetic field dependent optical response. We have computed interband optical conductivity $\sigma_{inter}(\omega)$ of $Y_2Ir_2O_7$ for (001), (111) and "all–in/out" orientations of moments. The results are shown on Fig.3 where one can see a very different behavior of this function depending on the imposed magnetic configuration at infrared frequencies. The intraband Drude contribution can also be restored from our computed intraband plasma frequencies for the metallic (001) and (111) states which are pretty small and equal to 0.7 and 0.2 eV, respectively. Thus, controlling the strength and direction of the applied magnetic field one can reach a continuous change from metallic to insulating response in this system.

Experiment finds that changing the A–site of $A_2Ir_2O_7$ will vary the properties considerably. Yanagishima and Maeno [22] show that for $A_2Ir_2O_7$, the electrical conductivities of A=Pr, Nd, Sm and Eu exhibit metallic behavior, while the electrical conductivities of A=Gd, Tb, Dy, Ho, Yb and Y are like in insulators. Matsuhira et al.[21] also observe that the A–site induces the change from metal to insulator, but they claim that it is taken
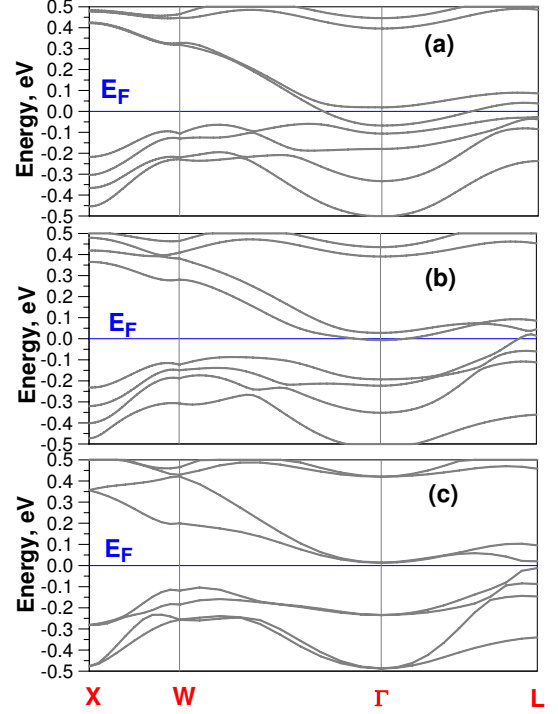

FIG. 2: LSDA+U+SO electronic band structure of $Y_2Ir_2O_7$ for different orientations of magnetic moments: (a) along (001) direction; (b) along (111) magnetization direction; (c) "all-in/out" configuration.
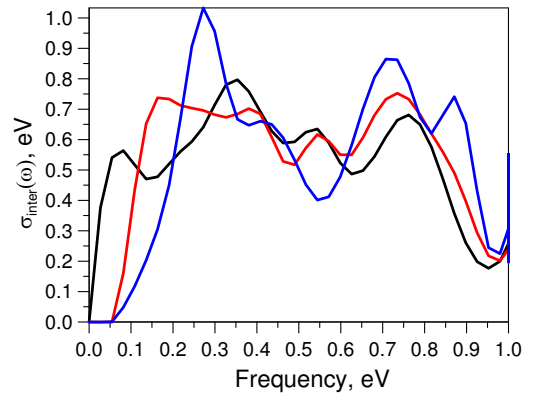

FIG. 3: Calculated interband optical conductivity of $Y_2Ir_2O_7$ for different orientations of magnetic moments: black – along (001) direction; red – along (111) magnetization direction; blue – "all-in/out" configuration.

place around Nd. Namely, the systems with A=Nd, Sm and Eu are insulators while those with A=Pr are metals. Matsuhira *et al.*[21] try to contribute this discrepancy to the quality of samples. However, even using the same synthesis condition, the discrepancy still appears[21].

To clarify the effect of A–site, we first perform a constrained calculation with the $4f$ band shifted by a constrained potential. This however almost does not affect the bands around the Fermi level. So, one can conclude that the rare earth element has a small effect on the conductivity. We further perform the calculation by using $A_2Ir_2O_7$ structure but replacing the rare earth element A by Y. Like in $Y_2Ir_2O_7$, the ground state is found to be "all–in/out" non–collinear solution. However for $Pr_2Ir_2O_7$ and $Nd_2Ir_2O_7$, the ground state is metallic. Changing the A–site from Nd to Sm and further to Eu results in decrease in the ionic radius. This reduces the Ir–O–Ir angle, and makes our calculation for A=Sm and Eu to produce insulating band structures. We contribute the discrepancy between Ref.[22] and Ref.[21] to the smallness of the energy difference between the "all–in/out" ground state and other metastable states.

In summary, using the LSDA+U+SO method, we have explored the electronic and magnetic properties of geometrically frustrated pyrochlore iridates. Our study reveals that the ground state of these systems has a non–collinear "all–in/out" magnetic configuration of moments. Our constrained calculation shows that the A site has a small affect on the energy bands near the Fermi level while different ionic radii and corresponding changes in lattice parameters are the reason why A=Pr are metallic while A=Nd, Sm, Eu, and Y are insulating. Thanks to the strong SO coupling in Ir $5d$ states, rotation of magnetization can produce insulator–to–metal transition thus making iridates to be interesting candidates for various applications, such, *e.g.*, as giant magnetoresistance effect and magnetooptics.

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